JOURNAL DE PHYSIQUE
Colloque C3, supplément au n°6, Tome 44, juin 1983

PHOTO INDUCED INFRARED ACTIVE PHONONS IN TRANS POLYACETYLENE

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Résumé - Nous avons mis en évidence des phonons actifs dans l'infrarouge dans le trans $(CH)_x$ par une technique d'absorption photoinduite. Il y a une corrélation avec une bande d'absorption photoinduite d'origine électronique. Nos résultats montrent la photoproduction de défauts libres chargés avec un temps de vie long.

Abstract - We measured photogenerated ir active phonons in trans-$(CH)_x$ by the photoinduced absorption technique. A correlation was found to exist with a photoinduced absorption band in which electronic transitions are involved. Our results show photoproduction of free charged defects with long lifetimes.

In the photoinduced optical absorption technique[1] (PA), the signal arises from the change $\Delta\alpha$ in the optical absorption spectrum of the semiconductor due to the presence of excited carriers. Recently, Orenstein and Baker[2] have reported measurements of the PA spectrum in $(CH)_x$ at a delay time of 10μsec following excitation, in the energy range 0.5eV to 1.6eV. In trans - $(CH)_x$ they observed two new subgap PA bands at 1.36eV and at 0.5eV. These bands appear to be uncorrelated to each other due to their different decay time and different temperature dependence[2]. Very recently the resultant interband bleaching at 2eV[3] and the PA spectrum from 1.2eV to 1.9eV[4] were measured with picosecond pulse excitation. It was shown that the gap states[4] and their resultant interband bleaching are produced in less then 10^{-13} sec and that the photogenerated carriers are localized but highly mobile[3].

In this work we report the steady state PA spectrum in trans $(CH)_x$ in the energy range 0.09 to 1.1 eV, which includes also the phonons energy range[5]. The photoinduced changes in the sample optical absorption spectrum were measured with an incandescent light source dispersed by a monochromator. The light transmitted through the sample(T) and its changes (ΔT) were measured with a solid state detector having a wide spectral range. The laser beam used for excitation was a CW Ar^+ with photon energy of 2.4eV which is larger than the gap of trans-$(CH)_x$. Phase detection techniques improved the sensitivity of $\Delta T/T$ to 10^{-5} for most parts of the spectrum. The sample was in the form of thin film of $(CH)_x$ grown on NaCl substrate, initially polymerised as cis-$(CH)_x$ and subsequently isomerized to trans-$(CH)_x$.

In Fig. 1 the induced absorption ($-\Delta T/T$) at 10K obtained with a laser absorbed power of $20mWcm^{-2}$ is plotted versus the probe photon energy. The PA spectrum consists of an assymetric band peaked at 0.43 eV with a FWHM of 0.35eV and a much narrower doubly peaked feature with maxima at 170meV($1360cm^{-1}$) and 157meV($1256cm^{-1}$) with FWHM of less than 4meV ($32cm^{-1}$). At higher temperatures these bands decrease in intensity and shift up in energy (172meV and 0.48eV at 200K). We identify the narrow PA bands as induced ir active phonons, due to their energy location[6,7] and sharpness[5]. The broader assymetric PA band is due to electron transitions from photoinduced localized states in the gap (with a delta function energy distribution)

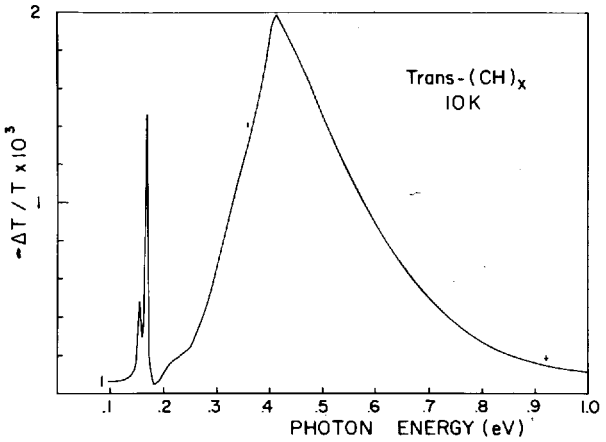

Fig.1 - Photoinduced absorption spectrum. $\Delta\alpha \simeq 2.5\times10^{5}\Delta T/T$.

to the nearest band edges (with an almost square root singularity in a quazi 1D system like $(CH)_x$) However we note that this band is sharper than half the width of the interband absorption of trans-$(CH)_x$ (which is about 1.5eV). The lack of induced bleaching ($\Delta\alpha<0$) in the whole energy range below the gap shows that the induced localized states cannot be associated with ionization of ingap natural impurities. Also the lack of induced bleaching in the energy range of the natural ir active phonons located in trans-$(CH)_x$ at 1015 cm^{-1} and at 3000 cm^{-1}, shows that the photoinduced phonons to not take their large oscillator strength from the C-H vibrations. Both PA bands (the electronic and the vibronic) derive their strength directly from the π-π^* transitions. In fact we observed (not shown in Fig. 1), photoinduced bleaching for $\hbar\omega$ above E_g which we could associate with the appearance of the new PA bands. This proves that these bands are intrinsic in origin[2-4].

The PA bands at 0.43 eV and at 0.15-0.17 eV share a common origin since their absorption strength $\Delta\alpha(=\alpha_L \Delta T/T, \alpha_L$ is the absorption coefficient at the laser frequency) exhibits similar dependencies on the laser intensity, laser chopper frequency and sample temperature. An example is shown in Fig. 2 where their intensities at 80K are plotted as a function of the laser chopping frequency; the PA strength for each lines saturates at about 200Hz. Since $\Delta\alpha=N_s\sigma$ (where N_s is the steady state density and σ is the defect absorption cross-section), this frequency dependence shows that steady state condition is reached only at about 5×10^{-3} sec, implying that the recombination lifetime is longer than 10^{-3} sec at 80K. We measured the dependence of $\Delta\alpha$ on the laser intensity-I(Fig.3). $\Delta\alpha$ for both bands has a $I^{\frac{1}{2}}$ behaviour, characteristic of bimolecular recombination kinetics[1], followed by saturation at high intensities. The PA strength for both bands decreases with temperature: a slow decrease up to 150K, where the decrease becomes more pronounced. We conclude therefore that the electronic and the vibronic PA are due to the same photo-induced defects.

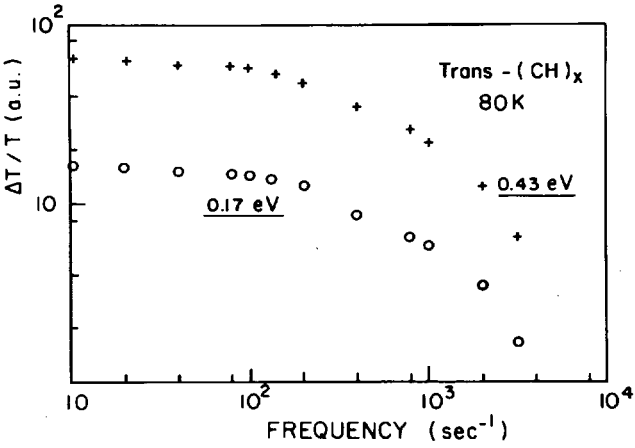

Fig. 2 - The dependence of $\Delta T/T$ on the laser chopping frequency.

We can estimate N_s shown in Fig. 1 assuming that the doping induced and the photo-induced defects have similar Σ. From the doping induced "midgap" absorption band[8] and the associated impurity density we evaluate the defect integrated absorption cross-section $\Sigma=\int\sigma dE\simeq4\times10^{-16}$ cm^2 eV. Integrating the 0.43eV absorption in Fig. 1, we

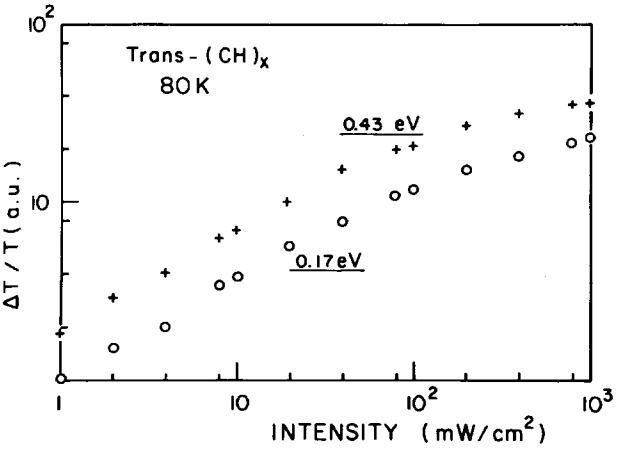

Fig. 3 - The dependence of ΔT/T at 80K on the laser intensity-I

calculate $N_s \simeq 6\times10^{17}$ cm^{-3}. From this we can estimate the generation quantum efficiency η of these defects, since $N_s = G\eta\tau$. Taking $\tau \simeq 5\times10^{-3}$ sec, η is of order 10^{-2}. This η is consistent with the decay in the picosecond time range which was interpreted as due to geminate recombination[4]; the induced signal in trans-(CH)$_x$ decays to 5×10^{-2} of its strength at t=0 in 1.5×10^{-9} sec at 80K[3].

The infrared activity in the phonon range in both photo-induced and doping induced cases[6], proves[7] that the induced defects are charged. However there is an important difference between the induced spectra in the phonon range obtained by the two different methods. In the earlier work[6] two strong ir active phonons were observed upon dilute doping in trans-(CH)$_x$: a narrow (50cm^{-1}) mode at 1370cm^{-1} and a broader (300cm^{-1}) mode at 900cm^{-1}. In more recent experiments[10] a third weaker vibration was observed at 1270 cm^{-1}. In the case of photogeneration we observe only the two high frequency vibrations (slightly shifted at 10K), namely at 1360cm^{-1} and at 1255 cm^{-1}. The 900cm^{-1} mode is completely missing from the PA spectrum (see Fig. 1). In their original work[11], Su, Schrieffer and Heeger interpreted the doping induced ir active vibrations as due to charged soliton vibrations. However the lower frequency mode at 900cm^{-1} was ascribed to vibrations of the soliton against the impurity, and therefore it is a pinned mode. Later, some contraversy about the origin of this mode appeared in the literature[6,7]. In our case the photoinduced defects are not connected to impurities and therefore should not be pinned. The failure to observe this mode in the photoinduced experiment confirms therefore that the 900cm^{-1} mode is indeed the pinned mode[7,11].

Based on B. Horovitz general analysis[7], we can tentatively associate each new ir active mode to phonons lines of C=C stretch character which are observed in Raman scattering. The 1360cm^{-1} line is the modifed 1470cm^{-1} C=C mode[5], the 1255cm^{-1} is the modified 1290cm^{-1} C-C mode[5] (which appears weaker in Raman scattering) and the strong 1090 cm^{-1} mode observed in Raman scattering[5] is shifted to frequency lower than 750cm^{-1} (our experimental lower limit) and is transformed into the pinned mode of the free defect which theoretically is shifted to ω=o.

Based on our calculation of N_s we can estimate the defect mass (a more precise calculation which is not based on N_s will be published elsewhere). The induced absorption strength $\Delta\alpha$ at 0.17 eV is about 350cm^{-1}; similar in strength to the absorption of the natural ir active phonons of trans - (CH)$_x$[9]. Taking $N_s = 6\times10^{17}$ cm^{-3}, the oscillator strength per induced defect is enhanced by more than 3 order of magnitudes as compared to the natural vibrations of this compound. A defect (or impurity) mode ir oscillator strength is inversly proportional to its vibrating mass[12]; We conclude therefore that the defect mass should be of order of m_e (electron mass).

Our results show that supergap light absorption in trans-(CH)$_x$ produces mobile, light mass charged defects with associated ingap localized states, whose lifetime is longer than few miliseconds. These findings may show indeed that free charged solitons are photogenerated in trans-(CH)$_x$[13] since they fit the expected soliton properties. However there are yet two unresolved problems in this picture

connected with our findings: (i) The electronic PA band is located at 0.43eV(with threshold at 0.25 ev), quite far from the expected soliton absorption at midgap(0.7 eV). (ii) The PA strength saturates at high light intensities; We estimate the saturation defect density to be $2\text{-}4\times10^{18}$ cm^{-3}. Solitons possess a reverse charge-spin relationship[11] and it was theoretically shown that photoinduced e-h pair decays to charged soliton-antisoliton pair (J.R. Schrieffer, Les Arc conference). Since our experiment definitely shows the existence of photoinduced charged defects, the crucial experiment needed now to prove solitons photogeneration in trans-$(CH)_x$ is to measure the unpaired spins photogeneration quantum efficiency. However the saturation at high illumination intensities and the small charged defects quantum efficiency certainly influence the conclusions of this crucial experiment. Preliminary results where these effects were taken into consideration (A. Heeger, Les Arc conference) suggest that this quantum efficiency is indeed small.

On the other hand our results might fit photoproduction of charged polarons. The energy threshold of the electronic PA at 0.25eV fits well the predicted low energy transition of the charged polaron in trans-$(CH)_x$[15,16]. However a second correlated transition at higher energy (1.1 to 1.4 eV), which was also predicted for charged polarons[15] was not found in the PA experiments (J. Orenstein et.al., Les Arc conference).

A part of this work was done at Brown University while one of us (Z.V.) was supported by the NSF MRL program and by NSF Grant; We thank Prof. J. Tauc for his kindly support, T. Kirst and D. Pfost for technical assistance and B. Horovitz for fruitful discussions.

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